

THE EFFECT OF CO₂ CLATHRATE HYDRATE ON THE OCEAN DISPOSAL OF CO₂: A REVIEW OF DOE-SPONSORED RESEARCH

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INTRODUCTION

Deep ocean disposal of CO₂ is an option to mitigate rises in atmospheric levels of CO₂ if other measures are ineffective and the worst global warming scenarios begin to occur. Through its Office of Fossil Energy, the U.S. Department of Energy (DOE) supports research directed at evaluating the feasibility of this option for long-term CO₂ disposal. Two projects, managed at the Federal Energy Technology Center (FETC) in Pittsburgh, Pennsylvania, are being conducted that specifically address the technical issues associated with deep-ocean disposal of CO₂. One of the projects is being conducted at FETC; the other at the University of Hawaii at Manoa (UHM) in Honolulu, Hawaii. The purpose of this paper is to describe the scope of these projects and summarize current experimental and theoretical results.

BACKGROUND

In 1993, a research needs assessment for capture, utilization, and disposal of CO₂ from fossil fuel-fired power plants was prepared for DOE by the Massachusetts Institute of Technology (1). This well-received report concluded that establishing the feasibility of large-scale disposal options should be assigned the highest research priority of all needs identified. Of the large-scale disposal options considered at that time, the principal ones were those using the deep ocean or deep confined aquifers for storage. With respect to ocean disposal, the key research recommendations focused on the impact of the CO₂ clathrate hydrate on the effectiveness of this disposal option.

Depth is a key factor in ocean disposal of CO₂. To avoid premature escape of the CO₂ from surface waters to the atmosphere, injection below a depth of about 500 m would be required. From approximately 500-m to 3000-m ocean depth, undissolved CO₂ would exist as a buoyant liquid. At greater depths, the liquid CO₂ would sink. In the absence of hydrate formation, the minimum depth for effective CO₂ sequestration would be around 700 m. Drops released at this depth would completely dissolve before reaching a depth of 500 m (1).

CO₂ clathrate hydrate (CO₂ · nH₂O, 6 < n < 8) is a crystalline compound that can form under temperature and pressure conditions associated with CO₂ disposal in the ocean below a 500-m depth. The hydrate can form either as solid crystalline particles or as a coating on the surface of liquid CO₂ drops. The solid hydrate particles should sink in the ocean, facilitating sequestration; however, thin hydrate shells on liquid CO₂ drops would limit dissolution of the CO₂ and complicate sequestration attempts. During transport to depth and injection, hydrate formation may clog submerged conduits, erode and foul injector nozzles, and negatively impact CO₂ dispersion. The U.S. DOE supports experimental and theoretical research at FETC and at UHM to address these concerns. A small high-pressure viewcell at FETC and a large pressurized tank at UHM are being utilized in the experimental programs. Mathematical modeling of these phenomena is also being performed at both FETC and UHM.

RESEARCH AT FETC

The work at FETC was initiated in 1993. All of the experimental work has been performed in a high-pressure, variable-volume viewcell (HVVC) that has a maximum working volume of about 40 cm³. A description of the HVVC system and basic experimental procedures have been published (2,3). The HVVC system can operate at temperatures down to near 0°C and at pressures up to 69 MPa (10,000 psig). The HVVC system can therefore be used to simulate ocean depths down to 6900 m. This is more than adequate for studying the behavior of CO₂ at the depths currently being considered for unconfined release of CO₂ in the ocean (1000 m to 1500 m) (4).

To enable more accurate prediction of the fate of CO_2 injected into the ocean, experiments at FETC have focused on determining the relative density of the hydrate in water (2,5) and seawater and on the formation of hydrate shells on drops of CO_2 and their effect on drop dissolution (2,6). With respect to the relative density of the hydrate, observations in two-phase systems with water and either gaseous or liquid CO_2 showed that the hydrates which formed at the $\text{CO}_2/\text{H}_2\text{O}$ interface were initially snowlike in appearance and buoyant in the water-rich phase. With time, the hydrates became icelike (transparent) in appearance and sank. Trapped, unconverted CO_2 may have caused the bulk density of the initially formed hydrates to be less than that of the water-rich phase. Eventually, this trapped CO_2 either escaped or was converted to hydrate, causing the density to increase and the appearance to change. In contrast, when formed from dissolved CO_2 , the hydrates were initially icelike in appearance and sank. Buoyant hydrate particles would frustrate sequestration in the ocean by causing the CO_2 to rise to unacceptably shallow depths. On the other hand, sinking hydrate particles would facilitate sequestration by causing the CO_2 to descend to greater depths before dissolution and thus increase its residence time in the ocean.

Some of the above experiments with water and CO_2 have recently been repeated using General Purpose Seawater (GPS) from Ocean Scientific International Ltd. As in the fresh-water experiments, hydrates formed from CO_2 dissolved in the seawater were icelike in appearance and sank in the seawater-rich phase.

Observations of the rate of hydrate shell formation on CO_2 drops in water and seawater have also been performed at FETC. In these experiments, a CO_2 drop is introduced into the viewcell and comes in contact with either existing hydrate particles or the glass or stainless steel parts of the viewcell itself. In all such cases, hydrate shell formation began at the point where the bubble or drop contacted the crystalline hydrate or viewcell, then rapidly spread out along the bubble or drop surface. Others have also reported similar phenomena (7). Specific examples from our experimental work have been previously described (6). The rate of growth of the hydrate shell on CO_2 drops (0.5 cm to 1 cm in diameter) in water has been estimated at 0.5 to 1.0 cm^2/s . Recent observations in seawater gave similar results.

The rate of dissolution of hydrate-covered CO_2 drops has also been studied in water (2) and more recently in seawater. In these experiments, the rate of decrease in drop radius was measured. Rates in the range of 0.0045 to 0.02 cm/h have been observed for hydrate-covered drops. These rates are slower than those obtained by other workers (2). The differences between the results are likely due to dissimilar experimental conditions and equipment. Data from the recent experiments in the viewcell indicate that the rate of shrinkage of CO_2 drops in seawater appears to be slower than in fresh water for drops of similar size under similar conditions. The reason for the slower rate in seawater is the topic of current investigations.

To overcome the limitations of the viewcell and more realistically simulate the environment that a CO_2 drop encounters in the ocean, a high-pressure water tunnel facility has been planned. This device is patterned after a similar apparatus developed by others for the study of methane hydrates (8). A low-pressure model is currently under construction to verify the flow patterns in the proposed test section of the tunnel.

Recent mathematical modeling efforts at FETC have been directed at determining the thickness of the hydrate shell that forms on CO_2 drops under conditions expected for ocean disposal (6). The model was developed to estimate both the thickness of the initially-formed shell and the bounds on the ultimate thicknesses of shells after reaching steady state in saturated and unsaturated environments. The degree of saturation is determined relative to the equilibrium CO_2 concentration at the hydrate equilibrium pressure, C_H , at the temperature of the system. Under anticipated ocean disposal conditions, the system can actually be oversaturated owing to the induction period that often accompanies hydrate formation (6).

The model assumes that the ultimate thickness of the shell is governed by the diffusion of the CO_2 through the hydrate shell and diffusion or convection of dissolved CO_2 away from the hydrate-covered particle. It was demonstrated that a very thin hydrate shell (<0.1 cm) would initially form around drops of injected CO_2 . If injected into unsaturated water, a stable hydrate thickness on the order of 10^2 to 10^4 times the radius of the drop would form. The model therefore implies that the initially formed shell would become thinner in an unsaturated environment. The thinning of the hydrate shell after formation has been experimentally observed in the viewcell experiments and is reflected by changes in both the texture and transparency of

hydrate-covered drops. Initially, the shell has rough texture and is opaque. Within a few minutes the shell becomes smooth and relatively transparent.

For a CO_2 drop injected into saturated water, the model predicts that with time the hydrate shell would thicken, possibly approaching 10^{-1} cm in thickness for growth periods well in excess of 100 hours. Such conditions could occur in the vicinity of the injection. Since the water is saturated with respect to hydrate-forming conditions, the hydrate shell serves only to slow the diffusion of CO_2 and thus limit the formation of additional hydrate from the injected CO_2 . Results for this scenario are shown in Figure 1. The diffusivity values for CO_2 through the hydrate shell, D_H , used in Figure 1 are in the range of values for diffusivities in solids. Experimental determination of this value would be required for validation of this portion of the model.

In water oversaturated with CO_2 relative to C_H , the shell could also thicken by addition to the hydrate layer from the CO_2 dissolved in the water. This mode of growth was the subject of an earlier paper (9). The above model also did not take into consideration the effect of varying salt concentration at the surface of drop as hydrates form. Current modeling efforts at FETC are directed at incorporating this effect.

RESEARCH AT UHM

A 36-month research grant to investigate ocean disposal of CO_2 was awarded by DOE to the University of Hawaii at Manoa in August 1995. The laboratory study is being conducted by the Hawaii Natural Energy Institute of the School of Ocean and Earth Science and Technology. The principal objective of the study is to obtain data on liquid CO_2 discharge jet instability and on drop dispersion, interactions, and dissolution under conditions representative of the deep ocean. These data will be applied to the development and validation of predictive models to perform (ocean) environmental hazard assessments and to devise injection methods that ensure effective containment of the CO_2 from the atmosphere.

Experiments at UHM employ a unique High-Pressure CO_2 Mixing Facility (HCMF), designed specifically to investigate the oceanic CO_2 disposal process. The HCMF comprises a cylindrical pressure vessel, systems to hold and supply liquid CO_2 and chilled (ambient to 0°C) water, and diagnostics and data acquisition equipment. The insulated steel pressure vessel has an I.D. of 0.55 m and is 2.46-m tall. During experiments, it is partially filled with fresh or seawater and pressurized with an inert gas to simulate conditions in the ocean down to depths of approximately 600 m. A photograph of the pressurized test vessel is shown in Figure 2. Numerous viewports provide access for quantitative optical probes and for flow visualization. Details of the construction and operation of the HCMF have been reported (10).

Two types of tests will be conducted using the HCMF: (1) continuous discharging of liquid CO_2 through a variety of orifices over a range of conditions to study effluent breakup and injector performance; and (2) monitoring of single CO_2 droplets or droplet pairs as they dissolve and interact during simulated buoyant rise through the ocean. In the continuous discharge experiments, a non-intrusive, laser scattering diagnostic will be employed to map droplet size distribution spectra, velocity, and number density in the region immediately downstream from the injector. These data on initial CO_2 droplet size distributions and spatial dispersion are needed to model accurately the disposal process. The primary experimental variables include jet velocity, simulated depth of discharge, and injector orifice size and geometry.

In the droplet dissolution experiments, a transparent diffuser will be submerged in the pressure vessel aligned with its vertical axis. Water from the vessel is pumped downward through the diffuser to stabilize in space buoyant liquid CO_2 droplets that have been bled into the diffuser. By this means, the unrestrained rise through the ocean can be simulated in a facility of finite height. Close-up image acquisition and analysis will be employed to document droplet dissolution and interaction phenomena.

In both the continuous discharge and dissolution tests, experiments will be repeated under ambient water conditions that either foster or preclude the formation of the CO_2 clathrate hydrate. As of this writing, facility preparations and diagnostic development are being completed.

Complementary mathematical modeling to date has focused on theoretical analyses of CO_2 jet instabilities and the generation of the dispersed droplet phase. The effects of hydrate formation on these instabilities have been considered (11). Results suggest that if hydrate formation

kinetics proceed more rapidly than the amplification of the jet instability, then breakup may be modified and the dispersed droplet phase size distribution altered. At the extreme, a solid hydrate layer could grow and deposit around the injection orifice, encasing the jet and possibly closing it off. While calculations indicate that hydrate formation effects will be restricted to situations involving relatively large injector orifices (> 1 -cm diameter) and low jet velocities (< 6 cm/s), the uncertainty in some parameters used in these calculations, notably the rate constant for hydrate formation, warrant experimental confirmation.

Recently, the DOE-funded experimental research at UHM has attracted international interest. Additional funds have been committed to the project by ABB Management, Ltd. in Switzerland and Statoil (Norway) has offered the use of instrumentation and the professional assistance of research personnel from the University of Bergen. Interest in collaborative studies has also been expressed by Japanese investigators.

SUMMARY

DOE-sponsored research at FETC and UHM is addressing important issues related to the effect of hydrates on the ocean disposal of CO_2 . These issues include: 1) the relative density of hydrate particles and how to either preclude hydrate formation or form particles that would sink in the ocean and thus facilitate sequestration efforts; 2) the behavior of hydrates during formation either as particles or as shells around liquid CO_2 drops, and how their formation would impact CO_2 dissolution and jet dynamics; and 3) the dissolution behavior of hydrate-covered CO_2 drops and the fate of these drops in the ocean. Data are being sought to help develop and validate predictive models which can be employed to identify effective sequestration strategies and to evaluate impacts on the marine environment.

DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. A Research Needs Assessment for the Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants, DOE Report DOE/ER-30194, July 1993 (available NTIS).
2. Warzinski, R. P.; Cugini, A. V.; Holder, G. D. Proc. Int. Conf. Coal Sci. 1995, 2, 1931-1934.
3. Warzinski, R. P.; Lee, C.-H.; Holder, G. D. J. Supercrit. Fluids 1992, 5, 60-71.
4. Omerod, B.; Angel, M. Ocean Storage of Carbon Dioxide: Workshop 2 - Environmental Impact, IEA Greenhouse Gas R&D Programme Report, June 1996.
5. Holder, G. D.; Cugini, A. V.; Warzinski, R. P. Environ. Sci. Tech. 1995, 29, 276-278.
6. Holder, G. D.; Warzinski, R. P. Prepr. Pap. -Am. Chem. Soc., Div. Fuel Chem. 1996, 41(4), 1452-1457.
7. Burruss as reported by E.D. Sloan, Jr. in International Conference on Natural Gas Hydrates; E.D. Sloan, Jr.; J. Happe; M.A. Hnatow, Eds.; Annals of the New York Academy of Sciences; Vol. 715; p 17.
8. Maini, B. B.; Bishnoi, P. R. Chem. Engng. Sci. 1981, 36, 183-189.
9. Holder, G. D.; Cugini, A. V.; Warzinski, R. P. Environ. Sci. Tech. 1995, 29, 276-278.
10. Masutani, S. M.; Kinoshita, C. M.; Nihous, G. C.; Ho, T.; Vega, L. A. Energy Convers. Mgmt. 1993, 34(9-11), 865-872.
11. Teng, H.; Masutani, S. M.; Kinoshita, C. M.; Nihous, G. C. Prepr. Pap. -Am. Chem. Soc., Div. Fuel Chem. 1996, 41(4), 1447-1451.

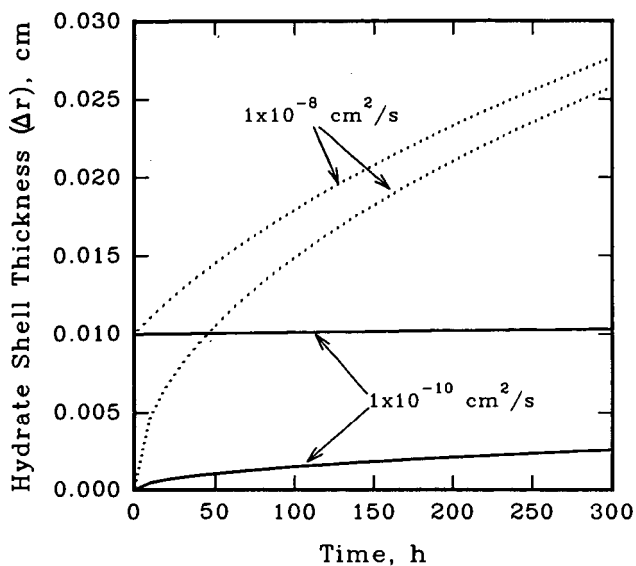


Figure 1. Thickening of the hydrate shell in a saturated reservoir as a function of time and solid-phase diffusivity, D_H (values shown in figure), and the initial thickness of the hydrate shell (indicated at time = 0).

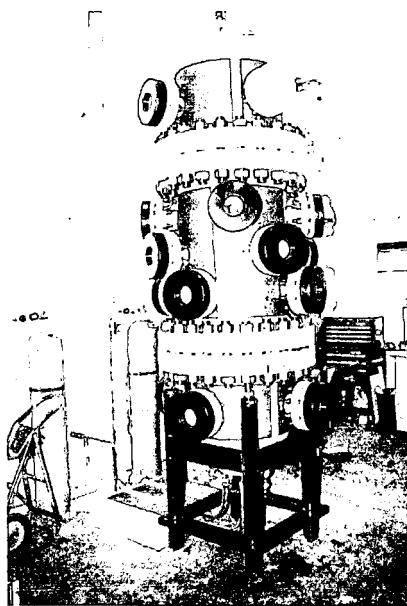


Figure 2. Photograph of the pressurized test vessel used in the High Pressure CO_2 Mixing Facility at the University of Hawaii at Manoa.